VOLTAMMETRIC STUDIES OF CYANOMETALATE COMPLEXES IN HIGHLY CONCENTRATED AQUEOUS SOLUTIONS

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Abstract: The electrochemical behaviour of the cyanometalate complexes $[Fe(CN)_6]^{4-}$ $[W(CN)_8]^{4-}$, $[Os(CN)_6]^{4-}$, $[Mo(CN)_8]^{4-}$ and $[Ru(CN)_6]^{4-}$ is investigated at high concentrations of the corresponding potassium salts (0.6 M) in alkaline solution (pH = 13) by voltammetric measurements with a platinum microdisk electrode. Under these experimental conditions the electrode reactions are reversible and the half-wave potentials are about 130 mV more positive than the standard redox potentials of these couples. The analytical characteristics of voltammetric determinations at high concentrations of electroactive species are studied using $K_4[W(CN)_8]$ as a model compound.

Key words: Cyanometalate complexes, microelectrode, voltammetry.

Introduction

Investigations of optical electron transfer processes between like charged reactants are very rare [1]. Outer-sphere metal-metal charge-transfer (MMCT) transitions in encounter complexes of free mobile hexacyanoferrate(III) and hexacyanometalate(II) (M=Fe,Os) and octacyanometalate(IV) (M=Mo,W) ions, respectively, in aqueous solution at high concentrations of the reactants have been observed recently in the visible and near-infrared spectral regions [2,3].

In order to gain further information on the free energy relationships within the reaction series the knowledge of the formal redox potentials of the couples involved in MMCT

under the conditions of the spectroscopic experiment (the total cyanometalate concentration equals 0.6 M, $[K^+]$ = 2.5 M, and $[OH^-]$ = 0.1 M [2,3]) is important. In such solutions voltammetric measurements with conventional sized working electrodes are complicated due to the extremely large currents that would result from the high concentrations of the electroactive species. In addition, the investigation of the highly concentrated cyanometalate solutions in a voltammetric cell of conventional size would consume considerable amounts of the high-added value noble metal complexes. Both problems can be solved by using a microdisk working electrode incorporated into a miniaturized voltammetric cell. In recent years a number of applications of microelectrodes in various fields of chemistry have been reported [4,5]. There are, however, only few papers dealing with electrochemical investigations in highly concentrated solutions addressing analytical aspects [6,7].

In the present work voltammetric studies with a microelectrode are applied to the characterization of a series of potassium cyanometalates at high concentration in aqueous solution.

Experimental

Apparatus

The voltammetric measurements were carried out at 25 °C with a computer-controlled electrochemical system ECM 700 (Center for Scientific Instrumentation, Berlin-Adlershof, Germany) and a Metrohm Model 506 potentiostat. The three-electrode arrangement was used throughout the investigations. The microdisk electrodes were prepared by direct glass sealing of 25 μm platinum wires (Goodfellow, Cambridge, GB). A platinum wire (0.5 mm in diameter) served as the auxiliary electrode and a saturated calomel electrode (SCE), connected with the cell via a glass capillary salt bridge, was used as the reference electrode. The cell body was a glass tube with an inner diameter of 10 mm. The necessary sample volume is about 0.5 ml.

Materials and Solutions

$K_4[Fe(CN)_6] \cdot 3 H_2O$ (Merck) and $K_4[Ru(CN)_6] \cdot 3 H_2O$ (Alfa) were recrystallized twice from methanol/water prior to use. $K_4[Mo(CN)_8] \cdot 2 H_2O$ [8], $K_4[W(CN)_8] \cdot 2 H_2O$ [9] and $K_4[Os(CN)_6] \cdot 3 H_2O$ [10] were prepared according to the literature. Stock solutions

(0.6 M) of the potassium cyanometalates were prepared by weight under exclusion of day-light using 0.1 M KOH in bidistilled water as solvent. The dissolution was facilitated by gradual warming to 50 °C.

Results and Discussion

Determination of half-wave potentials

Figure 1 shows the cyclic voltammograms for the octacyanotungstate system at scan rates of 25 mV/s and 25 V/s. A similar voltammetric behaviour was observed for the other systems and the results are summarized in Table 1.

At a scan rate of 25 mV/s quasi steady-state voltammograms (Fig. 1a) were recorded which indicate the high efficiency of mass transport to the microdisk electrode due to hemispherical diffusion. In contrast to this, at a scan rate of 25 V/s conventional peak-shaped cyclic voltammograms (Fig. 1b) are obtained indicating the predominance of linear diffusion. However, under the experimental conditions used there is still a contribution from spherical diffusion to the current signal [11]. The half-wave potentials obtained under steady-state conditions (v = 25 mV/s) are in good agreement (±5 mV) with that calculated according to $(E_{pa} + E_{pc})/2$ for high scan rates where E_{pa} and E_{pc} represent the anodic and the cathodic peak potentials, respectively.

The half-wave potentials $E_{1/2}$ (quoted vs. SHE) under the present conditions, except for $[Os(CN)_6]^{3-/4-}$, exceed the standard potentials E^0 by (130±10) mV. The similarity of the concentration-dependent redox potential shift may be interpreted in terms of similar ionic radii and equal charges of the complexes involved. The increase of the formal redox potentials of cyanometalates at high ionic strength (high concentration of cations) has been reported earlier [12-17] and attributed to the more extended ion-pair formation of the cyanometalates in the reduced forms than in the oxidized ones.

An apparently much smaller shift of $E_{1/2}$ vs. E^0, 65 mV, is observed for $[Os(CN)_6]^{3-/4-}$. The standard potential of this couple, however, has been estimated by a simple linear extrapolation to zero ionic strength from a plot of voltammetrically determined $E_{1/2}$ vs. $I^{1/2}$, where the ionic strength I was varied in the range of 0.1 to 1 M [14]. The standard potentials of the four other couples are based on determinations according to the reliable potentiometric approach employing both the oxidized and reduced component of the corresponding redox couple [12,13,15,16]. Thus, it seems to be reasonable to assume

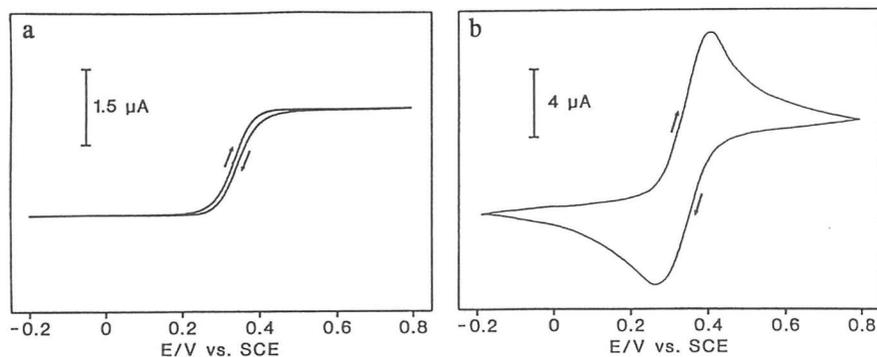that the standard potential of the $[Os(CN)_6]^{3-/4-}$ couple is by some 60 mV lower than that reported in [14].

Figure 1. Cyclic voltammograms recorded with (a) 25 mV/s and (b) 25 V/s in a solution containing 0.6 M $K_4[W(CN)_8]$ and 0.1 M KOH. The working electrode is a 25 µm platinum microdisk electrode.

Table 1. Half-wave potentials and Tomes $E_{3/4}$ - $E_{1/4}$ criterion for the heterogeneous electron-transfer rate of $[M(CN)_x]^{3-/4-}$ couples in 0.6 M aqueous solutions of $K_4[M(CN)_x]$, pH = 13, at 25 °C (M=Fe, Ru, Os, x=6; M=Mo, W, x=8).

M=	Fe	Ru	Os	Mo	W
$E_{1/2}$ / V (vs. SHE) a)	0.485	1.000	0.700	0.846	0.579
$E_{1/2}$ / V (vs. SHE) b)	0.484	0.995	0.699	0.843	0.576
$E_{1/2}$ / V (vs. SHE) c)	0.356	0.860	0.634	0.726	0.456
$E_{3/4}$ - $E_{1/4}$ / mV	58.2	56.4	56.0	55.6	56.4

a) from steady-state voltammograms, b) from peak potentials of cyclic voltammograms recorded with 25 V/s, c) standard redox potentials from References [12-16].

Electron-transfer characteristics

The electron-transfer kinetics of the redox processes was characterized using the Tomes criterion [18] which is based on the difference in potentials considering a steady-state voltammogram at the points where the current is one-quarter and three-quarters of the limiting diffusion current. For all redox couples the $E_{3/4}$ - $E_{1/4}$ difference was close to the theoretical value for a reversible one-electron process which is 56.5 mV (see Table 1). These results indicate a fast heterogeneous electron-transfer behaviour in the highly concentrated cyanometalate solutions. Recently several authors [19-21] have reported results on the influence of the cation of the base electrolyte and its concentration on the kinetics of highly charged redox couples. They concluded that at high concentrations of cations the electron-transfer reaction appears to be faster than at low concentration or in solutions without deliberately added supporting electrolyte. According to our investigations this is confirmed even if the potassium cyanometalate itself is the main source for the high concentration of cations.

Investigation of the analytical sensitivity at high cyanometalate concentrations

The concentration determination of electroactive substances can easily be derived from steady-state voltammograms recorded with microelectrodes in quiescent solutions. For measurements with a microdisk electrode the limiting current i_l is described according to Equation (1)

$$i_l = 2\,n\,F\,D\,c\,d \qquad (1)$$

where n=1 is the number of transferred electrons, F the Faraday constant, D the diffusion coefficient of the electroactive species, c its concentration and d the "effective" diameter of the microdisk electrode.

The electrochemically active surface area of the working electrode was derived from the limiting steady-state current obtained for a solution of $5 \cdot 10^{-4}$ M $K_4[Fe(CN)_6]$ in 0.1 M KCl assuming $D = 0.630 \cdot 10^{-5}$ cm^2/s [11]. An "effective" electrode diameter d = 27.0 µm was obtained.

The validity of Equation (1) at high concentrations was examined using $K_4[W(CN)_8]$ as a model compound. The analytical sensitivity, defined as the ratio between Δi_l and Δc in a narrow linear range of the calibration plot, was determined for concentrations up to 0.6 M cyanometalate in 1 M KCl. For concentrations lower than or equal to $6 \cdot 10^{-3}$ M the sensitivity was constant, however, at higher concentrations an unexpected change in sensitivity exhibiting a maximum value was observed as shown in Fig 2.
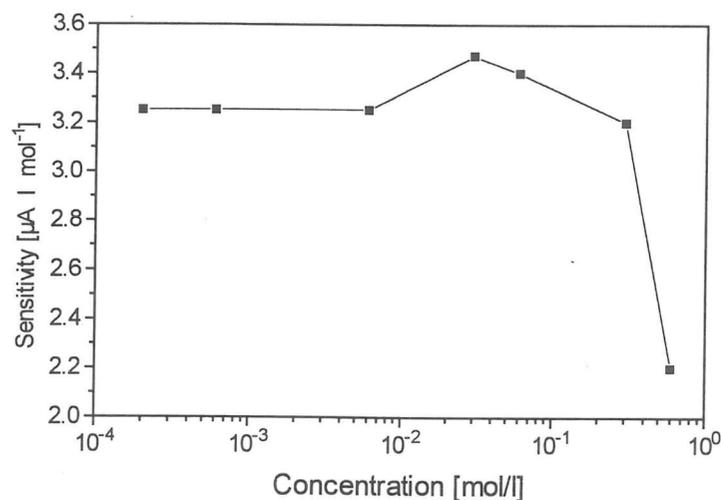

Figure 2. Analytical sensitivities in dependence on concentration of $K_4[W(CN)_8]$. The sensitivities were determined measuring the steady-state currents within the concentration intervals $[0.8 \cdot c \leq c \leq 1.2 \cdot c]$.

The changes in sensitivity result from changes of the diffusion coefficient of the electroactive species which is described by the Stokes-Einstein equation (2)

$$D = k\,T / 6\,\pi\,r\,\eta \qquad (2)$$

where k is Boltzmann's constant, η the viscosity of the solution and r the hydrodynamic radius of the diffusing species. The changes of the diffusion coefficient may be attributed

to both solvent viscosity effects (a relative viscosity of $\eta/\eta_0 = 1.44$ for 0.54 mol/kg aqueous $K_4[Fe(CN)_6]$ with respect to pure water at 30 °C has been reported [22]) and different hydrodynamic radii of the electroactive species in the differently concentrated solutions used here. These two effects are counteracting which results in the occurrence of a maximum sensitivity between $6 \cdot 10^{-3}$ M and $3 \cdot 10^{-2}$ M. In addition, for high cyanometalate concentrations the effect of migration on the total mass transport has to be taken into consideration.

Conclusions

It has been shown that in highly concentrated aqueous solutions the half-wave potentials of the cyanometalate couples under investigation are by some 130 mV more positive than the corresponding standard potentials. This allows for the estimation of the free energy gap contribution to the absorption maximum energies of a series of outer-sphere MMCT transitions between hexacyanometalate(II) (M= Fe, Ru, Os) and octacyanometalate(IV) (M= Mo, W) complexes, respectively, as donor components and $[Fe(CN)_6]^{3-}$ as the acceptor.

In addition, the heterogeneous electron-transfer behaviour in the highly concentrated cyanometalate solutions appears to be fast.

From the analytical point of view it is interesting that platinum microdisk electrodes can be applied to investigate the electrochemical properties of highly concentrated solutions of electroactive species without negative effects from the ohmic potential drop. At very high concentrations of cyanometalate complexes, however, attention has to be paid to deviations from the linear dependence of the limiting current on analyte concentration.

Acknowledgment

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